Discussion

Comparison of the equilibrium constants generated in this work with those generated by Allinger and Coke shows that the current values are approximately 10% lower at all temperatures. Yet the enthalpy and entropy of isomerization agree very well with their values of −2.72 ± 0.20 kcal/mol for ΔH and −0.55 ± 0.3 eu for ΔS and with the value of −2.69 ± 0.31 kcal/mol for ΔH measured by Speros and Rossini (*6*). The major reason for the observed differences is believed to be the fact that Allinger and Coke did not actually sample the liquid phase. Instead, they ran a batch reaction for a predetermined length of time and quenched the entire bomb thereby condensing all of the vapor phase into the liquid. They then corrected for this by using estimates of the vapor-phase composition. Systematic errors could have resulted from their extrapolation of the vapor pressure data of Camin and Rossini (*7*) well outside of the measured range and their use of calculated critical parameters.

A second possible source of error lies in the fact that their reaction products were quenched (thermally) in the presence of their catalyst thereby providing the opportunity for some catalytic reaction at lower temperatures resulting in a higher trans/cis ratio.

In the current study, liquid was withdrawn from the reactor at temperature and pressure in the absence of catalyst, thereby requiring no corrections. Since the differences in sampling technique could result in a reasonably constant variation between results from the two studies, almost parallel lines and hence similar values of ΔH would be expected. The small difference in slopes when extrapolated to $(1/T) = 0$ would also explain the similarity in values of ΔS.

Conclusions

The current equilibrium work with *cis*- and *trans*-decalin was done to verify that meaningful thermodynamic data on the hydrogenation of multiring aromatics in the liquid phase could be obtained with a newly designed equilibrium cell. In demonstrating this validity, equilibrium constants which are approximately 10% lower than previously published values were obtained. These differences notwithstanding, the resulting values for the enthalpy and entropy of isomerization were consistent with published values and differences in the values of equilibrium constants can be explained by differences in experimental technique.

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Transport Properties of a Long-Chain Molecule with Side Groups Capable of Molecular Orientation. Diffusion of Triolein in *n*-Alkanes at 25 °C

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Measurements of interdiffusion coefficients have been carried out for triolein (glycerol trioleate) in *n*-alkanes at 25 °C. The experimental results are compared to earlier measurements for 1-iododecane in *n*-alkanes, and the discussion is carried out briefly in a qualitative manner.

As a part of research projects at this Institute, extensive measurements of interdiffusion coefficients have been carried out (*1–3*) with the main interest directed toward the influence of the relative size of the solute and solvent molecules on the measured interdiffusion coefficients. The data reported in the present paper mark the end of this type of study.

Experimental Section

Triolein (glycerol trioleate, glycerol tris(*cis*-9-octadecenoate)) was a Fluka reagent-grade chemical. It was used as received.

Table I. Experimental Data for the Diffusion of Triolein in *n*-Alkanes at 25 °C

solvent	$10^7 D_0$, $\mathrm{cm^2\ s^{-1}}$	η_0, cP	$10^7 D_0 \eta_0$, dyn	V_m, $\mathrm{cm^3\ mol^{-1}}$
n-hexane	88.52	0.2985	0.2642	131.6
n-heptane	69.54	0.3967	0.2759	147.5
n-octane	55.08	0.5151	0.2837	163.5
n-decane	36.79	0.8613	0.3169	195.9
n-undecane	29.00	1.095	0.3176	212.2
n-dodecane	23.35	1.378	0.3218	228.6
n-tridecane	18.45	1.711	0.3157	244.9
n-hexadecane	11.89	3.095	0.3680	294.1
n-heptadecane	9.25	3.711	0.3433	310.5

The *n*-alkanes were the same as those used in previous studies (*1, 2*).

The method used for the measurements of the diffusion coefficients is that of free diffusion in which an initially sharp boundary is formed between a solution and its pure solvent.

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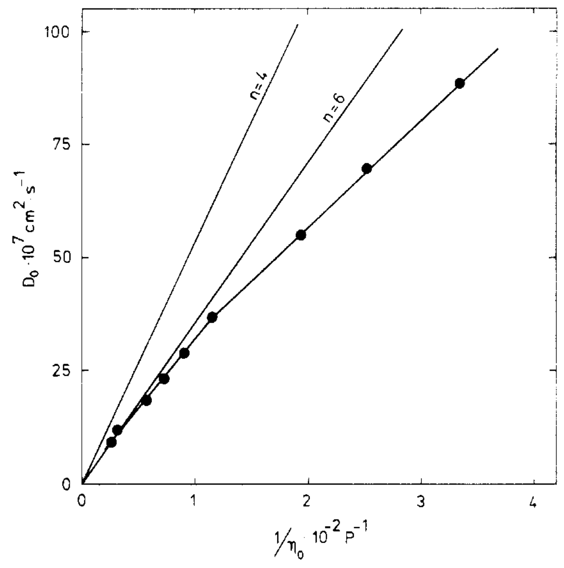

Figure 1. Plot of the limiting interdiffusion coefficient, D_0, against the reciprocal dynamical viscosity, $1/\eta_0$, of the solvent, for triolein in n-alkanes at 25 °C.

Details of the experimental arrangements, the method of measurements, and evaluation of the experimental results have been reported earlier (*1*). Since previous studies (*1–3*) have shown the diffusion coefficients of the organic solutes in n-alkanes to be essentially independent of concentration, even for concentrations of up to 6% by weight, solute concentrations of ~2% by weight were used in the present study. No extrapolations to infinite dilution were therefore carried out. The accuracy of the diffusion coefficients obtained by the measuring technique employed here has been estimated earlier (*1–3*) and is considered better than 1% for the data reported in this paper.

Results and Discussion

In Table I, the experimental results are summarized for the interdiffusion coefficients of triolein in n-alkanes at 25 °C. In Figure 1, the data in Table I are plotted as the limiting interdiffusion coefficient (D_0) against the reciprocal of the solvent viscosity (η_0). Figure 2 shows the plot of D_0 against $1/\eta_0$ for the diffusion of 1-iododecane in n-alkanes (*1*) at 25 °C. The relationship between D_0 and $1/\eta_0$ is given by the following modified form of the Stokes–Einstein equation (*4*):

$$D_0 = \frac{kT}{n \Pi \bar{r}_e} \frac{1}{\eta_0} \qquad (1)$$

where D_0 is the limiting interdiffusion coefficient, k is the Boltzmann constant, T is the absolute temperature, $\bar{r}_e$ is the equivalent hydrodynamic radius (for a nonspherical solute), η_0 is the solvent viscosity, and n is a factor which has been found to depend (*1*, *5–7*) on, among other things, the relative size of the solute and solvent molecules. Also shown in Figures 1 and 2 are two theoretical lines representing the two limiting values of n. The radii r_w = 6.18 Å for triolein and r_w = 3.68 Å for 1-iododecane, obtained by using the method of atomic volume increments (*8*), have been employed in the calculations of the slopes used in drawing the lines $n = 4$ and $n = 6$ in Figures 1 and 2. The shapes of the plots in Figures 1 and 2 are essentially similar, the only major difference being that the plot for triolein (Figure 1) apparently passes through the origin while that for 1-iododecane does not.

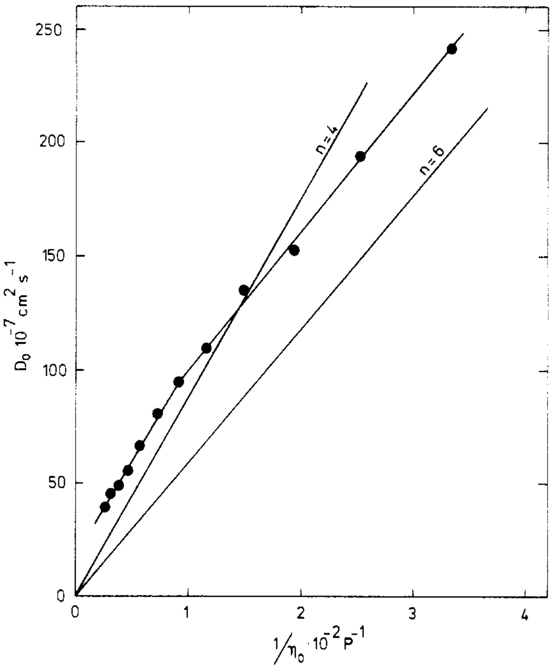

Figure 2. Plot of the limiting interdiffusion coefficient, D_0, against the reciprocal dynamical viscosity, $1/\eta_0$, of the solvent, for 1-iododecane in n-alkanes at 25 °C.

Glossary

D_0	limiting interdiffusion coefficient in $cm^2 \, s^{-1}$
k	Boltzmann constant
T	absolute temperature in K
n	factor characterizing the relative size of solute and solvent molecules
$\bar{r}_e$	equivalent hydrodynamic radius of solute molecule in Å (1 Å = 10^{-8} cm)
η_0	solvent viscosity in poise (1 P = 0.1 Pa s)

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